Conformation of adsorbed poly(vinyl pyrrolidinone) studied by infra-red spectrometry

J. C. Day* **and I. D. Robb**
Unilever Research Laboratory, Port Sunlight, Wirral, Merseyside L62 4XN, UK
(Received 1 March 1979; revised 14 June 1979)

The bound fractions of segments of PVP adsorbed on silica from chloroform and from deuterium oxide were estimated by the infra-red technique, using a Fourier transform spectrometer. 37 (±6)% of segments of the polymer adsorbed from chloroform were attached to the surface irrespective of molecular weight of the polymer or the level of adsorption. The bound fraction value obtained in deuterium oxide was lower and less reproducible than that in chloroform due to the small spectral shift which occurs on adsorption, but also exhibited no significant variation with coverage. A modification to the spectral analysis is suggested for systems involving small shifts. Comparison of the results with e.p.r. data on the same system indicated that, initially, the PVP molecules adsorbed onto the silica in a flat configuration, but at higher surface coverages, had more tails or loops.

INTRODUCTION

Knowledge of the conformation of polymer molecules adsorbed at the solid/liquid interface is essential in understanding their behaviour. Properties of the adsorbed layer such as the thickness and the number of attached segments have been measured by a variety of techniques[1,2]. If only one such property is measured, several average conformations of the adsorbed polymer may be compatible with the value obtained, but if two different properties of the adsorbed layer are measured, the conformation can be described more specifically. In this paper, the bound fraction, p, of poly(vinyl pyrrolidinone) (PVP) adsorbed on silica from deuterium oxide and chloroform is measured by infrared (i.r.) spectrometry[3,4] and compared with results previously obtained by electron paramagnetic resonance (e.p.r.) spectrometry on the same system[5].

Both methods distinguish between segments associated with the surface and those free in solution in loops or tails. However, p determined by i.r. is the fraction of segments in direct contact with the surface whereas that determined by e.p.r., a technique which relies on mobility differences, includes segments within 3 to 5 bonds of the attached segments[5,6]. The conformation of the adsorbed polymer molecules can be represented by a segment density distribution[7] (*Figure 1*), illustrating the difference in number of segments associated with the surface measured by each technique.

In applying the i.r. technique to PVP adsorbed on silica, the absorbance band due to the primary stretching vibration of the carbon–oxygen bond of the carbonyl group in the pyrrolidinone ring is monitored. When the polymer adsorbs, carbonyl groups interact with the surface hydroxyl groups to produce a band shift to a lower frequency[8]. The bound fraction is then calculated from the relative intensity of the shifted and unshifted bands.

EXPERIMENTAL

Two samples of PVP were dialysed against distilled water, freeze-dried, and stored over silica gel. Intrinsic viscosities were measured in water at 25°C and viscosity-average molecular weights calculated[9]. Characterization data for the polymer samples are summarized in *Table 1.*

The adsorbent ('Aerosil' silica, BET nitrogen area = 250 $m^2 g^{-1}$) was dried for 48 hours at 110°C, and stored over phosphorous pentoxide. During preparation of the adsorption mixtures, a standard procedure was followed to minimize variation in the hydration of the silica surface by atmospheric moisture. The solvents used were deuterium oxide (BDH) and chloroform ('AnalaR', 2% v/v ethanol)

Measured volumes of solvent and PVP solution of known concentration were added successively (total volume 5 cm^3) to a known weight (0.1 g) of silica in 10 cm^3 stoppered tubes. The mixtures were equilibrated at 23 (±2)°C for 60 h tumbling at 10 rpm. When the silica had settled, an aliquot (3 cm^3) of the supernatant solution was removed and the concentration of PVP in it was determined. In deuterium oxide, the absorbance of a PVP–iodine complex[10] at 500 nm (2×10^4 cm^{-1}) was measured, and in chloroform, the absorbance at 1675 cm^{-1} was monitored. The adsorption isotherm was calculated from these measurements.

The spectra of the silica suspensions (with and without adsorbed polymer), standard PVP solutions, solvents, and water-contaminated deuterium oxide (HDO in D_2O) were recorded in a silver chloride cell of pathlength 1.3×10^{-4} m, using a Cambridge Instruments Digilab FTS 14 Fourier transform infra-red spectrometer. The suspensions were thoroughly shaken immediately before the spectra were recorded and a standard procedure was followed to minimize variations due to sedimentation. All spectra were recorded against air as reference to eliminate the effects of water vapour in the light paths.

---

* Present address: The Broken Hill Proprietary Co. Limited, Central Research Laboratories, Shortland, NSW 2307, Australia

0032–3861/80/040408–04$02.00

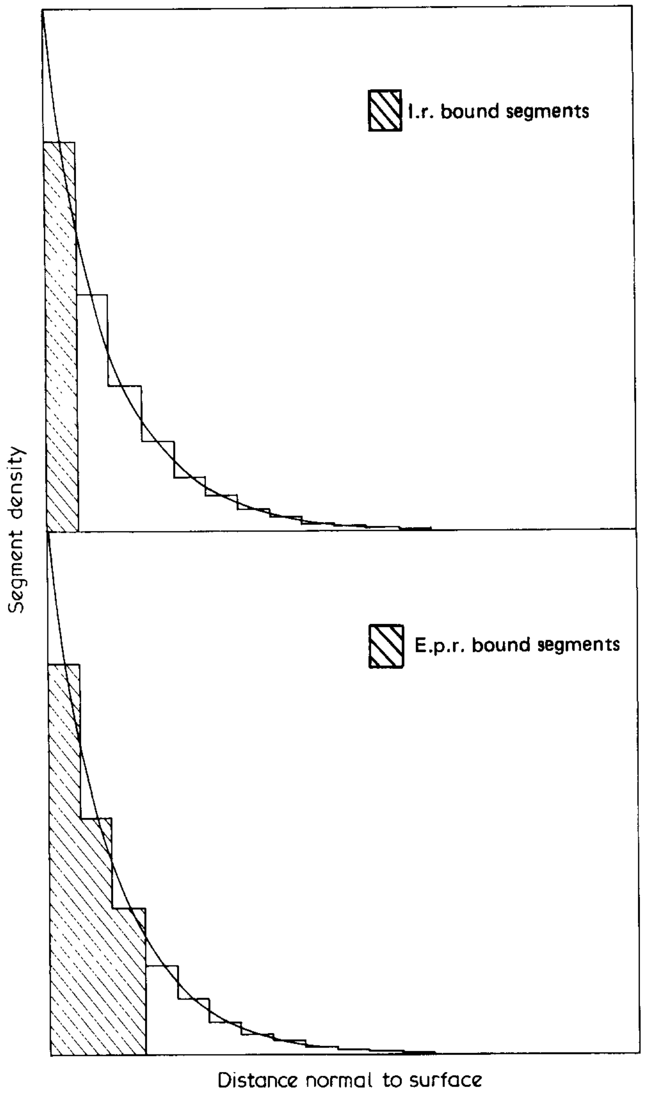

Figure 1 Segment density distribution for adsorbed polymers; hatched areas show segments associated with the surface as determined by each technique

TREATMENT OF DATA

In the model of the adsorbed polymer proposed by Fontana and Thomas[3] and developed by Thies, Peyser, and Ullman[4], the absorbance band of the functional group interacting with the surface is assumed to be resolvable into two bands – one representing segments not attached to the surface (in loops and tails) at the same frequency as segments of molecules free in solution, and another representing segments bonded to the surface (in trains) at a lower frequency.

The total concentration, C, of a suspension of polymer-covered adsorbent in polymer solution is:

$$C = C_S + C_{AF} + C_{AB} \tag{1}$$

where C_s is the concentration of polymer in the supernatant solution, C_{AF} is the concentration of free segments (loops and tails) of polymer in the adsorbed layer, and C_{AB} is the concentration of bound segments (trains) of polymer in the adsorbed layer. All concentrations are based on the suspension volume. The bound fraction, p, is then defined as:

$$p = \frac{C_{AB}}{C_{AF} + C_{AB}} \tag{2}$$

The absorbance, A, at any frequency in the region of the carbonyl stretching band is expressed as the sum of the absorbance of free segments in the adsorbed layer and in the supernatant solution, and the absorbance of bound segments in the adsorbed layer. At the frequencies, ν^0 and ν', corresponding to the maximum absorbance of the component bands representing free and bound segments respectively:

$$A^0 = \epsilon^0 Cl + (\epsilon^0_A - \epsilon^0)C_{AB}l \tag{3}$$

$$A' = \epsilon' Cl + (\epsilon'_A - \epsilon')C_{AB}l \tag{4}$$

where ϵ^0, ϵ' are the extinction coefficients for free segments at the two frequencies; ϵ^0_A, ϵ'_A are the extinction coefficients for bound segments at the two frequencies; and l is the coil pathlength. These two equations contain three unknown quantities: ϵ^0_A, ϵ'_A, C_{AB}. The ratio ϵ'_A/ϵ^0_A may be estimated by measuring a difference spectrum between adsorbed and free polymer such that the absorbance of unattached segments is nulled. This was first achieved experimentally by adjusting the concentration of the reference polymer solution[3,4], and later by using variable pathlength cells[11–18]. In the present investigation, the null curve is obtained by manipulating computer-stored spectra. The null curve (i.e. the absorbance band representing only the bound groups) yields the ratio of absorbances at the two frequencies of interest. This equals the ratio of the extinction coefficients of the bound groups at the two frequencies.

$$K = \frac{A'_{\text{Null}}}{A^0_{\text{Null}}} = \frac{\epsilon'_A C_{AB} l}{\epsilon^0_A C_{AB} l} = \frac{\epsilon'_A}{\epsilon^0_A} \tag{5}$$

Taking C_S from the isotherm, equations (3), (4) and (5) may be solved, and the bound fractions, p, calculated.

RESULTS

Figure 2 illustrates the component 'sample vs. solvent' spectra in deuterium oxide and chloroform which were required to isolate the carbonyl groups of the adsorbed PVP only (e.g. curves 'A' in *Figure 3*). Contributions to the suspension spectra from silica and solvent are removed first. *Figure 3* shows stages in the final subtraction of increasing proportions of the reference polymer solution spectra, which represents free carbonyl groups only, to obtain the null curve (curves 'B'), which represents the bound carbonyls only.

As illustrated for chloroform in *Figure 3*, the absorbance values, A^0 and A', required for equations (2) and (3), are

Table 1 Characterization data of polymer samples

Source	Sample designation	Intrinsic viscosity (dl g^{-1})	Viscosity-average molecular weight, $\bar{M}_v$
'Floresca' Field & Co. (Aromatics) Ltd, Middlesex, UK	PVP K40	0.2275	39 300
BDH Chemicals Ltd, Poole, UK	PVP K700	1.285	916 000

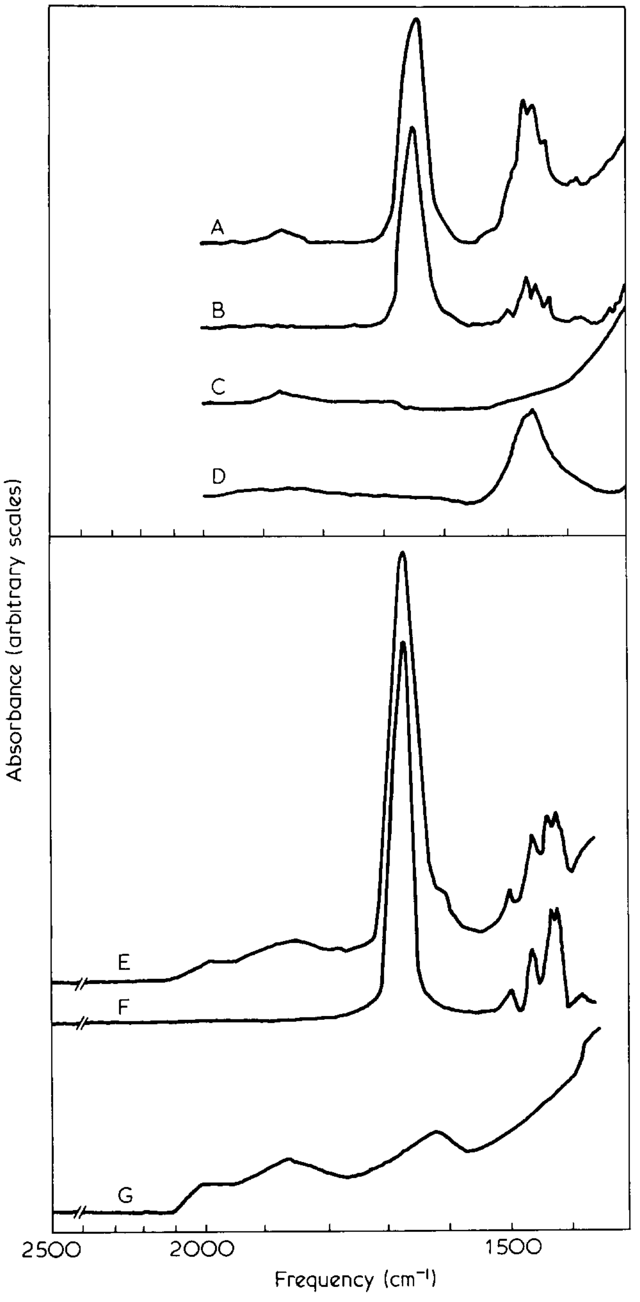

Figure 2 Examples of spectra (referenced against solvent) used to resolve the band due to bound carbonyl groups of PVP adsorbed on 'Aerosil' silica. A, PVP–silica–D_2O suspension; B, reference PVP–D_2O solution; C, dry silica suspension in D_2O; D, HDO in D_2O; E, PVP–silica–chloroform suspension; F, reference PVP–chloroform solution; G, untreated silica suspension in chloroform

obtained from curve A at frequencies $\tilde{\nu}^0$, = 1674 and $\tilde{\nu}'$, = 1655 cm^{-1}. These frequencies correspond to the maximum absorbance of the component bands representing free and bound groups, respectively. The factor, k, required for equation (5), is obtained from the ratio of the absorbance values on the null curve at the two frequencies. Since all other necessary data are known, equations (2), (3), (4) and (5) may then be solved for the bound fraction, p.

The subtraction of the reference PVP solution spectrum progressively removes the contribution from free carbonyl groups until a band representing only bound carbonyl groups remains at the null point. Determining the amount of the reference spectrum which must be subtracted presents some difficulty and two criteria were tested. The most commonly-used null criterion[4,11,12,16] illustrated by curves B in *Figure 3*, is that minimal negative deviation from the baseline should occur at frequencies greater than those of the band representing bound carbonyl groups only. This criterion is referred to here as No. 1. The assessment of this null point is subject to the judgement of the experimenter. In general, the larger the shift in the frequency of the absorbance band due to adsorption, the less subjective is the estimation of the null point. This is important in the estimation of the bound fraction of PVP on silica from deuterium oxide.

During subtraction of increasing proportions of the spectrum of the free carbonyl band in deuterium oxide from the compound band of free and bound carbonyl groups, a negative deviation in the resultant curve at the frequency of the free carbonyl band is observed in all cases (curves B, *Figure 3*). This negative deviation indicates overcompensation for the absorbance of free carbonyl groups. An alternative criterion, which will permit a better estimate of the bound fraction in deuterium oxide is based on the shape of the curve.

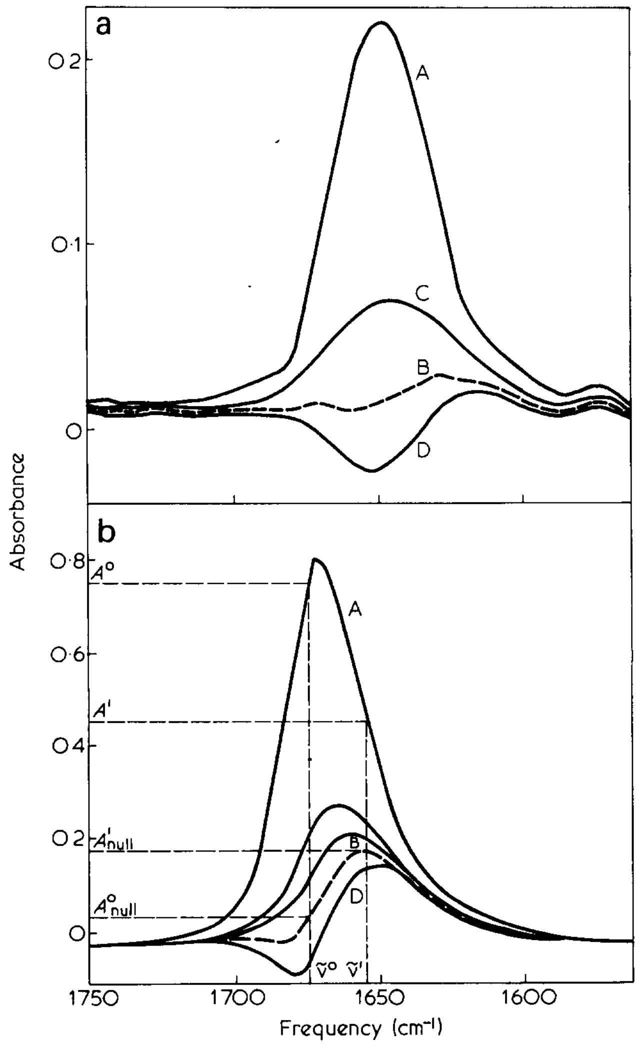

Figure 3 Typical series of spectra obtained during subtraction in each case of proportions of a reference PVP solution spectrum from the adsorbed polymer spectrum. (a) D_2O; (b) $CHCl_3$. A, Adsorbed polymer spectra; B, the null curves based on criterion No. 1; C, the null curve in D_2O based on criterion No. 2; D, over-compensated spectra

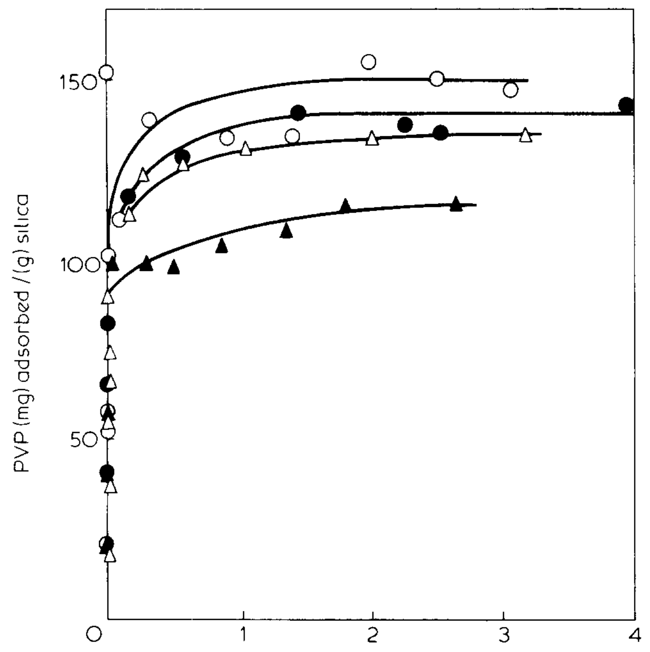

Figure 4 Adsorption isotherms of PVP adsorbed on 'Aerosil' silica from chloroform and deuterium oxide. ▲, Sample K40 from D_2O; ●, sample K40 from chloroform; △, sample K700 from D_2O; ○, sample K700 from chloroform

During the final subtraction, the difference spectrum shows a symmetric band with maximum absorbance about 5 to 10 cm^{-1} below the free carbonyl frequency (e.g. curve C in *Figure 3*). Thus an alternative null procedure for small shifts is to resolve the compound band of the adsorbed polymer into the two best-fitting symmetric bands. The free carbonyl band of the polymer in solution is symmetric (*Figure 2b*), so the alternative null point can be approached as usual by subtracting fractions of the spectrum of the free carbonyl band from the compound band until the difference spectrum shows maximum symmetry. This criterion is referred to here as No. 2. The symmetry can be measured, for example, by the ratio of half-widths at half the maximum intensity. In *Figure 3*, curve C is the null curve based on this procedure.

The adsorption isotherms and the variation of the bound fraction, p, with the fraction of the plateau adsorption attained, θ, are plotted for deuterium oxide and chloroform in *Figures 4* and *5*, respectively. The level of adsorption is similar in both solvents, showing a small dependence on the polymer molecular weight. This is consistent with behaviour frequently observed for polymer adsorption on to finely-divided silica where no special means have been used to disperse and stabilize the suspension[3–5,11–15].

The bound fraction values shown in *Figure 5* are those calculated from both null criteria. The values in both solvents did not alter greatly as the degree of adsorption or the supernatant concentration increased whereas those obtained by e.p.r. in the same systems[5] decreased with increasing θ.

The bound fraction values from both null criteria and the frequencies of the free and bound carbonyl bands are summarized in *Table 2*. When null criterion No. 2 is applied, the spectra obtained in deuterium oxide yield bound fraction values largely independent of θ. Criterion No. 2 cannot be applied to systems in chloroform as the degree of symmetry of the carbonyl band does not change before the null curve by criterion No. 1 is obtained.

DISCUSSION

The results in *Figure 5* show an important difference between the bound fraction values, p, determined by e.p.r. and i.r. spectrometry. By the former technique, p decreases with increasing θ, whereas by the latter it remains essentially constant. At low θ, (less than 0.5), $p_{\text{e.p.r.}}$ is nearly 1.0 whereas $p_{\text{i.r.}}$ is about 0.4, suggesting that the polymer is lying flat along its entire length, with about half the carbonyl groups directly bonded to the silica surface. At high θ, decreasing $p_{\text{e.p.r.}}$ indicates that the polymer chain is forming either longer loops or tails, but an almost constant $p_{\text{i.r.}}$ shows that a higher proportion of the segments close to the surface are actually attached to it.

Two factors favour longer tails over loops. Firstly, the increase in entropy from a given number of segments forming a tail (from lying in a flat adsorbed state) is greater than the same number forming larger loops. Secondly, the e.p.r. data[5] at high θ have been explained best by a simple two

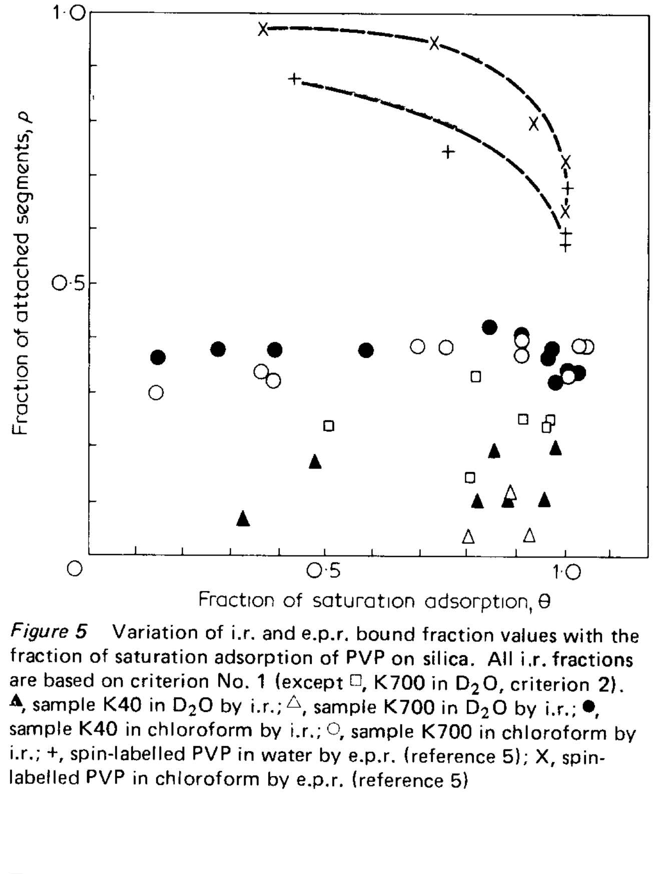

Figure 5 Variation of i.r. and e.p.r. bound fraction values with the fraction of saturation adsorption of PVP on silica. All i.r. fractions are based on criterion No. 1 (except □, K700 in D_2O, criterion 2). ▲, sample K40 in D_2O by i.r.; △, sample K700 in D_2O by i.r.; ●, sample K40 in chloroform by i.r.; ○, sample K700 in chloroform by i.r.; +, spin-labelled PVP in water by e.p.r. (reference 5); X, spin-labelled PVP in chloroform by e.p.r. (reference 5)

Table 2 Bound fraction values and carbonyl group band frequencies for PVP adsorbed from deuterium oxide and chloroform onto silica

Solvent		Deuterium oxide	Chloroform
Range of bound fraction value, p	By null criterion No. 1	0.03–0.20	0.30–0.43
	By null criterion No. 2	0.14–0.33	–
Free carbonyl frequency ($\tilde{\nu}^{\circ}$, cm^{-1})		1650 (±1)	1674 (±1)
Bound carbonyl frequency ($\tilde{\nu}^{1}$, cm^{-1})	By null criterion No. 1	1626 (±1)	1655 (±1)
	By null criterion No. 2	1644 (±2)	–

state model (mobile and immobile), to which contributions from intermediate segments (i.e. 2 or 3 from those bound) were negligible. If the polymer formed larger loops rather than tails, these intermediate segments would be important. Thus the data in *Figure 5* are best interpreted by the polymer lying flat over its whole length at low θ, with long tails being formed at higher θ. This behaviour is predicted[19] from computer simulation of macromolecules on surfaces, as the area per molecule is reduced. Similar qualitative conclusions can be drawn from PVP adsorption data in aqueous systems, though here the $p_{\mathrm{i.r.}}$ values are in more doubt because of the small shift of the carbonyl frequency on adsorption.

The conformation of adsorbed PVP deduced from these spectrometric measurements may be compared with that of PMMA adsorbed on silica from chloroform, to which the same techniques have been applied[4,6]. By the e.p.r. technique, all chain segments are immobilized in the adsorbed layer[6], but by the i.r. technique, only 25–30% are actually attached to the surface[4]. From this, the adsorbed conformation is interpreted to be flat, consisting of trains, and short loops and tails. However, neither the e.p.r. nor the i.r. bound fraction values alter with changes in θ. Thus the adsorbed conformation is flat not only at a low density of molecules on the surface (low θ), but also at the greatest density experimentally obtained ($\theta = 1.0$).

Studies of the different behaviour and competitive adsorption[6] of PVP and PMMA adsorbed on silica from chloroform showed that PVP was able to displace 50% of the PMMA adsorbed, though at high θ, PVP formed long tails whereas PMMA remained flat. This was tentatively attributed to the different flexibilities of the two polymers on the basis that the more rigid one (PVP) would have fewer segments in contact with a rough surface. The results of the current work show that the bound fraction of PVP is slightly greater than that of PMMA, in agreement with theoretical predictions[20,21].

The small differences between the frequencies of the carbonyl stretching band in aqueous solution and adsorbed on silica is the main reason for the unsuitability of the infra-red technique for studying the adsorption of polymers containing this group in such a system.

It is expected[22] that the frequency of the adsorbed carbonyl group will be independent of the solvent from which the polymer is adsorbed, supporting the use of null criterion No. 1 from chloroform and No. 2 from deuterium oxide, that is, the two criteria that avoid overcompensation for the free carbonyls. However, it is possible that the frequency of the adsorbed carbonyl group may be different in deuterated and protonated solvents, a hypothesis which might be checked by using deuterated chloroform as a solvent. Thus the infra-red technique can easily distinguish between attached and unattached segments of an adsorbed polymer, though quantifying the fractions in each state is more complex than has been mentioned in previous similar studies.

CONCLUSION

Infra-red spectrometry has provided a method for estimating the fraction of carbonyl segments (p) of a polymer, adsorbed at the solid/liquid interface, that are in direct contact with the surface. The criteria for separating the spectra of the bound and unbound segments depends on the magnitude of the spectral shift between these two groups. The results show that the fraction of segments of PVP adsorbed onto silica from chloroform did not vary significantly with polymer molecular weight or level of adsorption. This is in contrast to the value of p determined by e.p.r. on the same system, where it decreases with increasing coverage. Taken together these results suggest that at low coverage the polymer is lying flat on the surface, with approximately alternate groups being attached to the surface. At higher coverage the polymer formed long loops or tails, with an increasing proportion of the 'train' segments in direct contact with the surface. Tails seem more likely to form than loops from entropy considerations and from interpretation of the e.p.r. spectra. The major difficulty in using i.r. to study polymers adsorbed onto silica from aqueous systems is that the spectral shift is small.

REFERENCES

1 Stromberg, R. R. in 'Treatise on Adhesion and Adhesives', Vol. 1 (Ed. R. L. Patrick) Marcel Dekker, NY, 1967, p 69
2 Vincent, B. *Adv. Colloid Interface Sci.* 1974, **4**, 193
3 Fontana, B. J. and Thomas, J. R. *J. Phys. Chem.* 1961, **65**, 480
4 Thies, C., Peyser, P. and Ullman, R. 'Proc. 4th Intern. Congr. Surf. Act', Brussels, 1964, p 1041
5 Robb, I. D. and Smith, R. *Eur. Polym. J.* 1974, **10**, 1005
6 Robb, I. D. and Smith, R. *Polymer* 1977, **18**, 500
7 Silberberg, A. *J. Chem. Soc. Faraday Discuss.* 1975, **59**, 203
8 Rochester, C. H. *Powder Technol.* 1976, **13**, 157
9 Frank, H. P. and Levy, G. B. *J. Polym. Sci.* 1948, **10**, 371
10 Campbell, H. and Hunter, G. *The Lancet* 1953, 147
11 Thies, C. *J. Phys. Chem.* 1966, **70**, 3783
12 Peyser, P., Tutas, D. J. and Stromberg, R. R. *J. Polym. Sci. (A-1)* 1967, **5**, 651
13 Botham, R. A. and Thies, C. *J. Colloid Interface Sci* 1969, **31**, 1
14 Herd, J. M., Hopkins, A. J. and Howard, G. J. *J. Polym. Sci. (C)* 1971, **34**, 211
15 Killman, E. and Strasser, H. J. *Angew. Makromol. Chem.* 1973, **31**, 169
16 Morrisey, B. W. and Stromberg, R. R. *J. Colloid Interface Sci.* 1974, **46**, 152
17 Joppien, G. R. *Makromol. Chem.* 1975, **176**, 1129
18 Dietz, E. *Makromol. Chem.* 1976, **177**, 2113
19 Clark, A. T. and Lal, M. *J. Chem. Soc. Faraday Trans. II* 1979,
20 Clark, A. T., Lal, M., Turpin, M. A. and Richardson, K. A. *J. Chem. Soc. Faraday Discuss.* 1975, **59**, 189
21 Lal, M., Turpin, M. A., Richardson, K. A. and Spencer, D. *ACS Symp. Ser.* 1975, **8**, p 16
22 Bellamy, L. J., 'Adv. Infra-Red Group Frequencies', Methuen, London, 1968, p 151